

# Fuel and Additive Characterization for HCCI Combustion

*S. M. Aceves, D. Flowers, J. Martinez-Frias, F. Espinosa-Lopez, W. J. Pitz, R. Dibble*

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# Fuel and Additive Characterization for HCCI Combustion

Salvador M. Aceves, Daniel Flowers, Joel Martinez-Frias,  
Francisco Espinosa-Loza, William J. Pitz  
Lawrence Livermore National Laboratory

Robert Dibble  
University of California Berkeley

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## ABSTRACT

This paper shows a numerical evaluation of fuels and additives for HCCI combustion. First, a long list of candidate HCCI fuels is selected. For all the fuels in the list, operating conditions (compression ratio, equivalence ratio and intake temperature) are determined that result in optimum performance under typical operation for a heavy-duty engine. Fuels are also characterized by presenting Log(p)-Log(T) maps for multiple fuels under HCCI conditions. Log(p)-Log(T) maps illustrate important processes during HCCI engine operation, including compression, low temperature heat release and ignition. Log(p)-Log(T) diagrams can be used for visualizing these processes and can be used as a tool for detailed analysis of HCCI combustion.

The paper also includes a ranking of many potential additives. Experiments and analyses have indicated that small amounts (a few parts per million) of secondary fuels (additives) may considerably affect HCCI combustion and may play a significant role in controlling HCCI combustion. Additives are ranked according to their capability to advance HCCI ignition. The best additives are listed and an explanation of their effect on HCCI combustion is included.

## INTRODUCTION

HCCI is a combustion process that has some advantages with respect to both spark-ignited engines and diesel engines. HCCI combustion has been identified as a global autoignition process [1]. This is significantly different to the flame propagation that occurs in a SI engine, and it is also very different to the stratified combustion of diesel engines. Considering the great differences between these combustion processes, it is natural to expect that the fuels that have been optimized for SI engines and diesel engines may not be optimum for HCCI engines.

One of the advantages of HCCI combustion is its intrinsic fuel flexibility. HCCI combustion has little sensitivity to fuel characteristics such as lubricity and laminar flame speed. Fuels with any octane or cetane number can be burned, although the operating conditions must be adjusted to accommodate different fuels, which can impact efficiency. An HCCI engine with variable compression ratio or variable valve timing could, in principle, operate on any hydrocarbon or oxygenated liquid fuel, as long as the fuel is vaporized and mixed with air before ignition.

The literature shows that HCCI has been achieved with multiple fuels [2-4]. The main fuels that have been used are gasoline, diesel fuel, propane, natural gas, and single- and dual-component mixtures of the gasoline primary reference fuels, PRF (iso-octane and n-heptane). Other fuels can be used and some have also been tested to a lesser extent (methanol, ethanol, acetone). Previous research has shown that it is not optimal to use familiar fuel parameters such as octane or cetane ratings to guide in the definition of performance ratings of fuels for HCCI combustion [5]. Therefore, a better approach and a new set of ratings are needed to identify attractive fuels for HCCI engines.

In addition to the opportunity of identifying optimum fuels for HCCI combustion, there is also the opportunity of identifying optimum additives for HCCI combustion. Experiments and analyses have indicated that small amounts (a few parts per million) of secondary fuels (additives) may considerably affect HCCI combustion and may play a significant role in controlling HCCI combustion [6-9]. While it may be impractical to carry two fuels on board of a vehicle, it may be possible to manufacture the additive in the vehicle [7,10]. Otherwise, the additive may be stored in the vehicle and replenished at maintenance intervals. This is more likely if the additive is used in small quantities.

This paper presents an analysis of fuel and additive characterization for HCCI combustion. First,

different fuels are tested for predicting the maximum power output and efficiency that can be obtained within the constraints of peak cylinder pressure and combustion timing. The purpose is to compare different fuels for any given set of engine requirements (efficiency and power output).

The paper also shows Log(p)-Log(T) diagrams generated for four different fuels. Log(p)-Log(T) diagrams show chemical heat release rates as a function of temperature and pressure. Log(p)-Log(T) diagrams can be used to explain the behavior of fuels under different HCCI operating conditions. The four fuels used for the analysis include a fuel with little low temperature heat release (iso-octane), a fuel with substantial heat release at low temperature (n-heptane), and two fuels with equal research octane number (RON) and different chemical structure (n-pentane and a primary reference fuel, PRF, both with a 61.7 RON).

Finally, the paper shows how additives can be ranked according to their capability to advance HCCI ignition. It has been discovered that a very low concentration (10 ppm) of the best additives can advance HCCI combustion by almost 11 crank angle degrees. This is a big effect, equivalent to heating the charge by over 30 K, and it offers potential for successful control of HCCI engines.

## FUEL CHARACTERIZATION

Fuel characterization for HCCI combustion is conducted by performing multiple runs with a detailed chemical kinetics code running in single zone mode. Single zone runs assume that the air and fuel mixture is perfectly homogeneous in composition as well as temperature, and are expected to predict ignition timing with good accuracy [11]. On the other hand, single zone models are known to overpredict peak cylinder pressure [11]. HCT [12] is used for all the runs presented here. Two detailed mechanisms are used. A small mechanism with 179 species and 1125 reactions is used for all the short-chain fuels and a big mechanism with 913 species and 3620 reactions is used for iso-octane. The mechanisms are available on our website [13].

Parameters defining engine geometry and speed are listed in Table 1. These parameters are used for all the calculations in this paper. Table 2 shows engine operating conditions specific to the calculations described in this section. These conditions are representative of heavy-duty engines running at maximum power. The compression ratio is kept as a free parameter, while the intake temperature and equivalence ratio are adjusted to meet two constraints: the maximum heat release occurs at 5°ATDC, and the peak cylinder pressure is less than 250 bar. The inlet temperature can be varied in the range between 300 and 400 K, and the equivalence ratio has a maximum value of 0.5 to limit NO<sub>x</sub> emissions. Compression ratio is varied between 12 and 20. Intake pressure and engine speed are kept constant (3 bar absolute and 1800 rpm). A constant fraction of residual gases is

assumed (2 %). Composition of the residual gases is calculated assuming full combustion of the fuel into CO<sub>2</sub> and H<sub>2</sub>O. The charge temperature at intake valve closing is determined by a published procedure [14]. This procedure considers the mixing of residuals with fresh gases as well as the expansion during blowdown, but it does not take into account heat transfer to the wall. A long list of likely HCCI fuels is analyzed, including propane, methane, natural gas, methanol, hydrogen, ethanol and iso-octane.

Table 1. Engine geometry and operating conditions for all the single zone chemical kinetics runs conducted in this paper.

Parameter	Description
Stroke	10 cm
Bore	10 cm
Connecting rod length	15 cm
Speed	1800 rpm

Table 2. Engine operating parameters used in the fuel characterization section of the paper (Figures 1-4).

Parameter	Description
Intake pressure	3 bar absolute
Intake temperature range	300-400 K
Compression ratio range	12-20
Equivalence ratio range	0-0.5
Crank angle for peak heat release	5° ATDC
Maximum peak cylinder pressure	250 bar
Residual gas fraction	0.02
Heat transfer to walls	adiabatic

The results are presented in Figures 1-4. Figures 1 and 2 respectively show the intake temperature and the equivalence ratio that are necessary to obtain 250 bar of maximum pressure when maximum heat release occurs at 5°ATDC. Figure 1 shows temperature as a function of compression ratio. The figure shows that temperature is a decreasing function of compression ratio. Increasing the compression ratio reduces the amount of heating required for satisfactory combustion timing. Figure 1 also shows that the temperature for satisfactory combustion increases monotonically with octane number. The fuel with the lowest octane number among the fuels considered (iso-octane, RON=100) requires the coolest operating temperature, and the fuel with the highest octane number (methane) requires the highest operating temperature.

Figure 2 shows the equivalence ratio necessary to obtain the required ignition timing and peak cylinder pressure, as a function of compression ratio. The figure shows that equivalence ratio is a decreasing function of compression ratio. This trend is similar to the trend obtained for temperature in Figure 1. However, Figure 2 shows that the equivalence ratio lines for all fuels behave very similarly, with all of

them falling in a narrow band along the diagonal of the figure.

Figures 1 and 2 show the likely range of compression ratios that can be used for the different fuels over typical HCCI combustion. Iso-octane is limited to relatively low compression ratios, especially for the high intake pressure considered here. Use of iso-octane at high compression ratios may require cooling of the intake charge. On the other hand, methane and natural gas are limited to high compression ratio engines. Use of methane at low compression ratios may require considerable heating of the intake (over 400 K intake temperature), and this may prove impractical under many conditions.

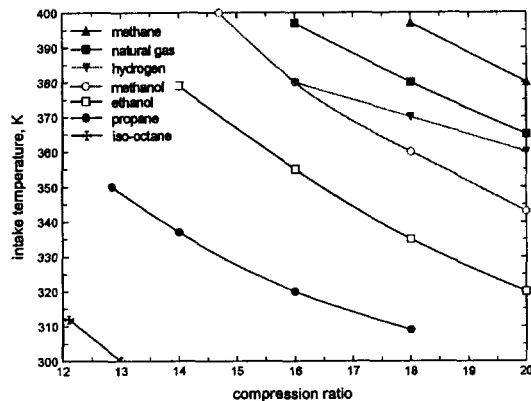


Figure 1. Intake temperature necessary to obtain 250 bar of maximum pressure when maximum heat release occurs at 5°ATDC as a function of compression ratio, for all the fuels being considered.

Figures 3 and 4 respectively show engine indicated efficiency and engine indicated mean effective pressure (IMEP) as a function of compression ratio, for all the fuels being considered. Figure 3 shows that efficiency is an increasing function of compression ratio, and Figure 4 shows that IMEP is a decreasing function of compression ratio. IMEP is a decreasing function of compression ratio because the peak cylinder pressure has to be kept under 250 bar. Meeting this restriction requires reducing the equivalence ratio as the compression ratio is increased.

Figures 3 and 4 also show that the lines for all fuels fall within a relatively narrow band of efficiency and IMEP. However, within the narrow band significant differences are observed. In Figure 3, natural gas and methane have about 4% lower efficiency than other fuels (ethanol, methanol). Methane and natural gas have a higher equivalence ratio than the other fuels for a given compression ratio (Figure 2). As a result, the specific heat ratio ( $\gamma$ ), is lowest for methane and natural gas, resulting in lower engine efficiency. Figure 4 shows that hydrogen falls noticeably below the IMEP-compression ratio line followed by all the other fuels. This is because burn

duration is extremely short for hydrogen, resulting in a high peak cylinder pressure. Considering that the engine has a restriction on peak cylinder pressure (250 bar), an HCCI engine running on hydrogen is limited to operate at a low equivalence ratio (Figure 2), resulting in a low IMEP.

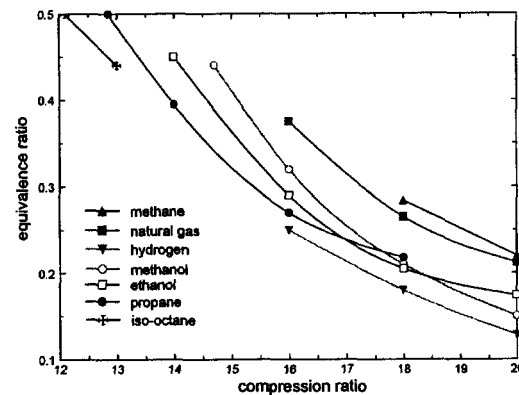


Figure 2. Equivalence ratio necessary to obtain 250 bar of maximum pressure when maximum heat release occurs at 5°ATDC as a function of compression ratio, for all the fuels being considered.

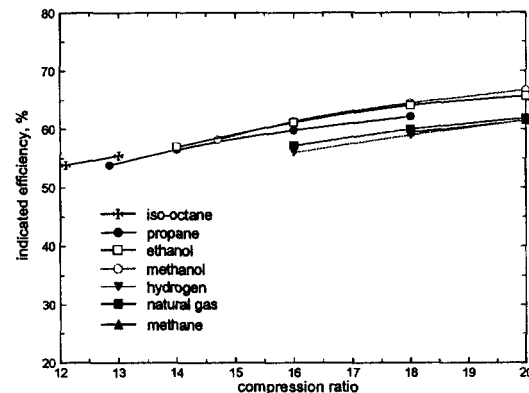


Figure 3. Engine indicated efficiency as a function of compression ratio, for all the fuels being considered.

One of the greatest challenges of HCCI engines is their low power output. Power output is typically limited by the peak cylinder pressure that the engine can withstand. In HCCI engines, combustion is very sudden, producing a high peak cylinder pressure that limits the power output that can be obtained from the engine. It would be desirable to find fuels with a longer burn duration that may result in higher power output. However, Figure 4 shows that no such fuel was identified in this analysis. The effect of the different fuels on maximum IMEP is relatively small.

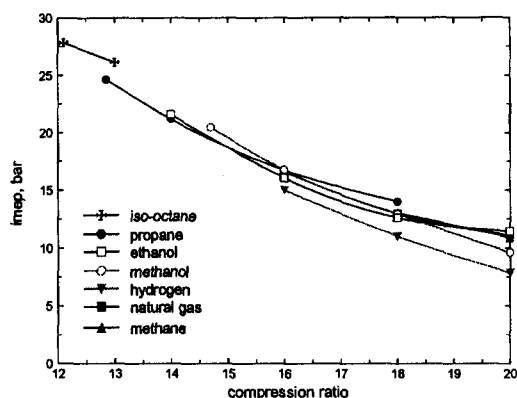


Figure 4. Engine indicated mean effective pressure (IMEP) as a function of compression ratio, for all the fuels being considered.

## HEAT RELEASE AND IGNITION IN HCCI ENGINES

Engine processes are well visualized in Log(p)-Log(T) diagrams. The benefits of using these diagrams have been extensively discussed in a recent publication [15], where the procedure was titled "visual thermodynamics." As described in [15], many diesel engine processes can be easily illustrated in Log(p)-Log(T) diagrams, including compression, combustion, expansion, ignition, white smoke generation, etc. Log(p)-Log(T) diagrams also have applicability to illustrate HCCI engine processes leading to autoignition.

This section shows Log(p)-Log(T) diagrams for four different HCCI fuels. These include a fuel with high octane number (iso-octane), a fuel with low octane number (n-heptane), and two fuels with the same research octane number (RON) but different composition (n-pentane and a primary reference fuel, PRF, both with a 61.7 RON). All the calculations presented in this section are performed with a detailed chemical kinetic code in single zone mode [12]. A detailed mechanism is used that contains iso-octane as well as n-heptane. This mechanism includes 1036 chemical species and 4238 chemical reactions. The analysis considers the engine dimensions listed in Table 1 and the engine operating conditions listed in Table 3.

The Log(p)-Log(T) diagrams for the four fuels are shown in Figures 5-8. These diagrams include three types of lines, described next.

**Compression lines.** These lines show the temperature and pressure history during the compression stroke. Twenty-one runs were conducted for each fuel by varying the intake temperature between 300 K and 500 K at intervals of 10 K. Figures 5-8 generally include three compression lines out of the 21 compression lines that were calculated. One for the lowest intake temperature considered in the analysis (300 K), one

for the lowest intake temperature for which ignition occurs, and one for the highest intake temperature (500 K). For n-pentane and n-heptane, the fuel ignites even when the intake temperature is 300 K so only two compression lines are presented. Compression lines appear as straight lines in Log(p)-Log(T) diagrams, up to the point where significant chemical heat release occurs.

Table 3. Engine operating parameters used in the heat release and ignition section of the paper (Figures 5-8).

Parameter	Description
Intake pressure	1 bar absolute
Intake temperature range	300-500 K
Compression ratio	16
Equivalence ratio	0.3
Residual gas fraction	0.02
Heat transfer to walls	adiabatic

Contour lines for chemical heat release rate. Heat release is calculated as a function of pressure and temperature during the compression stroke. Contour lines are then generated by interpolation between the heat release values calculated on the compression lines. Heat release is calculated in Watts per gram of fuel and then plotted in the Log(p)-Log(T) diagrams over the whole range of operation between the minimum and the maximum temperature.

**Ignition line.** This is the line at which high temperature (fast) combustion starts during HCCI compression. The ignition line is determined by finding the points at which the concentration of  $H_2O_2$  reaches a maximum. According to a previous publication [16], HCCI ignition occurs when the  $H_2O_2$  molecule decomposes into two OH radicals.

Figure 5 shows the Log(p)-Log(T) diagram for n-heptane. This is typical of low octane number fuels, in which there is a significant amount of chemical heat release at a relatively low temperature (800-900 K). Heat release reaches a maximum at an intermediate temperature (the cool flame region) and then drops as the temperature increases. High temperature ignition then occurs as the temperature is further increased. This is typically called two-stage ignition [17]. Low temperature heat release is so intense for n-heptane that even the coldest case ( $T_{in}=300$  K) reaches ignition. Low temperature heat release is most intense at high pressure, and therefore has a bigger effect on cases with a low intake temperature. Compression lines deviate from linearity very early in the process. The ignition line is almost a horizontal line, indicating that pressure has a very small effect on ignition for n-heptane. This is in agreement with the ignition lines plotted in [15], which were obtained from experiments done on a constant volume combustion vessel with cetane fuel.

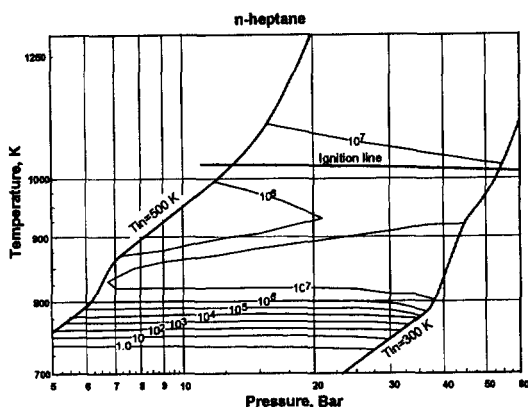


Figure 5. Log(p)-Log(T) diagram for n-heptane under HCCI compression conditions. The figure shows two compression lines, one for  $T_{in}=300$  K,  $p_{in}=1$  bar and another for  $T_{in}=500$  K,  $p_{in}=1$  bar. Compression lines show the temperature and pressure history during the compression stroke. The figure also includes multiple heat release contour lines. These lines show chemical heat release as a function of pressure and temperature, in Watts per gram of fuel, in powers of 10. Finally, the figure includes an ignition line, which is the line at which high temperature (fast) combustion occurs during HCCI compression.

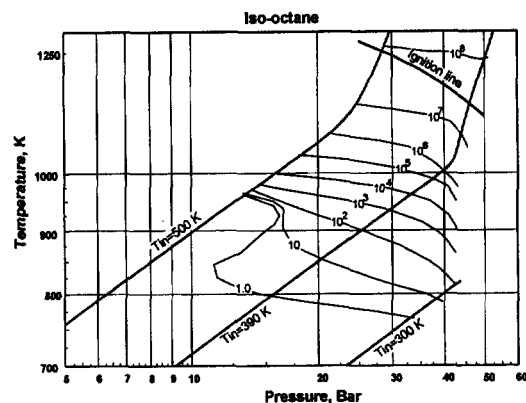


Figure 6. Log(p)-Log(T) diagram for iso-octane under HCCI compression conditions. The figure shows three compression lines, one for  $T_{in}=300$  K,  $p_{in}=1$  bar; other for  $T_{in}=390$  K,  $p_{in}=1$  bar (the lowest temperature to achieve ignition) and another for  $T_{in}=500$  K,  $p_{in}=1$  bar. Compression lines show the temperature and pressure history during the compression stroke. The figure also includes multiple heat release contour lines. These lines show chemical heat release as a function of pressure and temperature, in Watts per gram of fuel, in powers of 10. Finally, the figure includes an ignition line, which is the line at which high temperature (fast) combustion occurs during HCCI compression.

Figure 6 shows a Log(p)-Log(T) diagram for iso-octane. Iso-octane has very little early heat release, and no cool flame region. Considerable heat release occurs only as the compression temperature approaches the ignition line. The initial temperature has to be raised to 390 K before ignition occurs. Pressure has a considerable effect on ignition of iso-octane, as shown by the non-horizontal ignition line.

Figures 7 and 8 show the Log(p)-Log(T) diagrams for two fuels with the same research octane number (RON) and different composition. One is n-pentane (Figure 7) and the other is a primary reference fuel (PRF) with a 61.7 RON (Figure 8). Figures 7 and 8 are qualitatively similar but quantitatively different. Both show cool flame regions, but these are considerably smaller than for n-heptane (Figure 5). Cool flame regions in Figures 7 and 8 exist only at high pressure (over 20 bar). They therefore affect only cases in which the intake temperature is relatively low.

Figures 7 and 8 show that n-pentane has considerably more low temperature heat release than the 61.7 octane PRF, even though both have the same RON. For n-pentane, ignition is achieved even at the lowest intake temperature (300 K). For the PRF, the minimum intake temperature for ignition is 330 K. On the other hand, the compression line for  $T_{in}=500$  K is virtually identical for the two fuels. These lines are also similar to the  $T_{in}=500$  K compression line for iso-octane (Figure 6), indicating that there is very little low temperature heat release when the intake temperature is high.

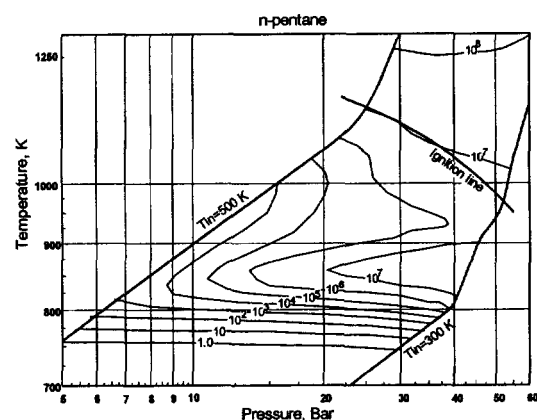


Figure 7. Log(p)-Log(T) diagram for n-pentane under HCCI compression conditions. The figure shows two compression lines, one for  $T_{in}=300$  K,  $p_{in}=1$  bar and another for  $T_{in}=500$  K,  $p_{in}=1$  bar. Compression lines show the temperature and pressure history during the compression stroke. The figure also includes multiple heat release contour lines. These lines show chemical heat release as a function of pressure and temperature, in Watts per gram of fuel, in powers of 10. Finally, the figure includes an ignition line, which is the line at which high temperature (fast) combustion occurs during HCCI compression.

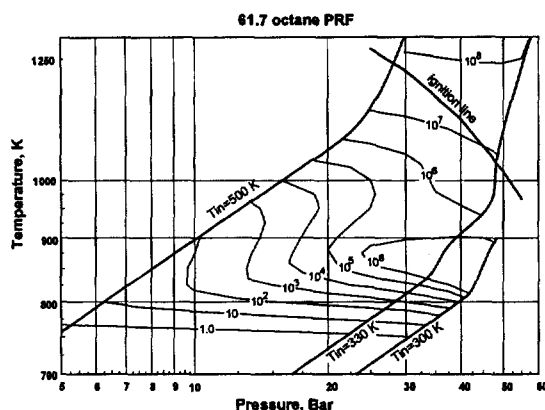


Figure 8. Log(p)-Log(T) diagram for a 61.7 PRF under HCCI compression conditions. The figure shows three compression lines, one for  $T_{in}=300$  K,  $p_{in}=1$  bar; other for  $T_{in}=330$  K,  $p_{in}=1$  bar (the lowest temperature to achieve ignition) and another for  $T_{in}=500$  K,  $p_{in}=1$  bar. Compression lines show the temperature and pressure history during the compression stroke. The figure also includes multiple heat release contour lines. These lines show chemical heat release as a function of pressure and temperature, in Watts per gram of fuel, in powers of 10. Finally, the figure includes an ignition line, which is the line at which high temperature (fast) combustion occurs during HCCI compression.

## ADDITIVE CHARACTERIZATION

Additive characterization for HCCI combustion is conducted by performing multiple runs with a detailed chemical kinetic code running in single zone mode. HCT [12] is used for all the runs with a detailed mechanism for iso-octane that includes 913 species and 3620 reactions. The mechanism is available on our website [13]. An initial run was made for a baseline condition typical of HCCI combustion with iso-octane fuel. Table 1 lists the geometric characteristics of the engine and Table 4 lists the operating conditions for the baseline run. The potential applicability of different species for advancing HCCI combustion is then evaluated by making 913 additional HCT runs. In each of these runs, the concentration of each of the 913 species is increased by 10 ppm with respect to the concentrations used for the baseline run. The timing for maximum heat release is then evaluated for each run and compared to the timing of the baseline run. This calculation allows us to rank the applicability of all 913 species for advancing the ignition timing and therefore evaluate their potential use as additive for controlling HCCI combustion.

The detailed chemical kinetic model has been validated by comparing predicted species concentrations to measured species concentrations in flow reactors and jet-stirred reactors at elevated pressures [18]. However, it is not possible to validate the model with respect to many of the 913 species in the mechanism because their concentration is too small or their lifetimes are too short to be experimentally measured. In particular, we have not been able to directly validate the

mechanism for alkylhydroperoxide peroxy radicals, ketohydro-peroxides, and alkylhydroperoxides additives, which are discussed below. The best available estimates for rate of production and consumption of these species have been put into the detailed chemical kinetic mechanism.

Table 4. Engine geometry and operating conditions for the additive evaluation section of the paper.

Parameter	Description
Intake pressure	1 bar
Intake temperature	410 K
Compression ratio	16:1
Equivalence ratio	0.3
Fuel	Iso-octane
Crank angle for peak heat release, baseline	6.4°
Residual gas fraction	0.02
Heat transfer to walls	adiabatic

Many of the 913 species in the mechanism are classified as unstable. Species are defined as unstable if their concentration drops by more than 1% during the first 10 crank angle degrees of the compression stroke. It is considered that species that decompose rapidly at near ambient conditions cannot be successfully stored or generated in the vehicle, and therefore have little practical applicability for HCCI engine control. Many radicals that are known to have an effect on HCCI ignition [15] are unstable (H, OH, O). According to this definition, 343 species out of the 913 species in the mechanism are found to be unstable. It should be noted that the stability definition used here is not very strict, and some unstable species may meet the requirement imposed. This is further discussed in the results.

The remaining 570 species are ranked according to how effectively they advance combustion with respect to the baseline run. Table 5 shows the results. The table shows the five species that have the greatest effect on advancing the time for maximum heat release, as well as a number of selected species that may be of interest because they are simpler species that could possibly be generated or stored in the vehicle. The table also includes the combustion timing obtained by increasing the intake temperature by 20 K, 30 K and 40 K with respect to the base case, for comparing the relative effect of additives with the effect of temperature.

Alkylhydroperoxide peroxy radicals are most effective at advancing combustion. They occupy most of the top 100 places in the ranking of fuel additives for advancing combustion. Some peroxides advance combustion by more than 11 crank angle degrees. This is a big advancement in combustion for a very small concentration (10 ppm). To obtain the same advancement in combustion, the intake temperature would have to be increased by over 30 K. Ozone is also very effective in advancing combustion, and can be generated on board a vehicle by a simple electrochemical reaction



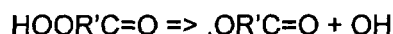
[7]. Ketohydroperoxides occupy most of the ranks between 100 and 200, advancing combustion between 6 and 8 crank angle degrees. Nitrogen compounds can also play a role as HCCI additives [6]. These include nitric oxide, which has previously been proposed as an HCCI additive [9]. Hydrogen peroxide ( $H_2O_2$ ) is not as effective as other additives, but  $H_2O_2$  may be easier to store and distribute [8].

The intake fuel concentration at the baseline conditions listed in Table 4 is 0.5% by volume or 5000 ppm. Therefore, the molar rate of consumption of additive at 10 ppm would be 500 times less than the molar rate of fuel consumption. It may therefore be reasonably easy to store the additive on a vehicle, provided that it is stable and environmentally benign. Ultimately, the benefit of using additives to control combustion has to be contrasted to the possibility of adjusting the intake temperature to obtain satisfactory combustion [19, 20].

Among the 913 potential additives that were used in this analysis, many were found that could considerably advance combustion, but none was found that could significantly delay combustion. The maximum ignition delay is less than 0.1 degrees, which is insignificant for practical purposes. Additives that delay combustion are mainly inert species. For inert species, combustion is delayed mainly through thermal effects (by decreasing the value of the specific heat ratio,  $\gamma$ , reducing compression heating). The chemical effect of additives considered in this work for inhibiting the reactions leading to HCCI ignition is negligible. However, other substances not considered in this analysis (fire retardants, i.e. bromine) may have a considerably greater effect in delaying HCCI combustion. Their stability and toxicity have to be evaluated before they can be applied for HCCI combustion control.

## THE CHEMICAL KINETICS OF HCCI ADDITIVES

The most effective additives in Table 5 for advancing combustion are the alkylhydroperoxide peroxy radicals. These species have the general molecular structure of  $HOOROO$ , where R is a hydrocarbon molecular structure. Additives labeled 1 through 5 in Figure 9 are in this family of additives. The reason why these species are particularly effective is because of the reactive sequence:



where R' is R minus one H atom. Note the production of two reactive OH radicals for the consumption of one alkylhydroperoxide peroxy

radical. These species are among the few additives considered that produce two OH radicals. If these radical species were being considered for generation on board a vehicle, their lifetime on time scales and temperatures appropriate for additive generation and storage would need to be estimated. Additional reactions, beyond what is in the current reaction mechanism for HCCI combustion, would need to be considered.

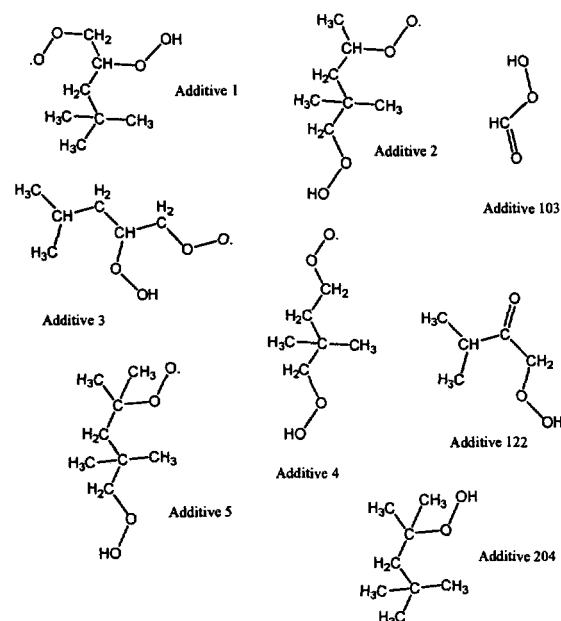


Figure 9: Molecular structure of selective additives. Each additive is identified by its ranking number (Table 5).

Ozone is a very effective additive due to the reaction:



Ozone's decomposition is slow enough so that it is stable during the early stages of the compression stroke but its decomposition increases rapidly with increasing temperature, providing O atoms to initiate the low temperature chemistry of iso-octane [7].

The HNO radical is effective in advancing combustion due to its decomposition to form reactive H atoms:



Table 5. Ranking of the different species according to their effect in advancing combustion in HCCI combustion, at the conditions detailed in Table 4 for the baseline run. Calculation assumes that 10 ppm of each additive are added to the composition of Table 4. For the baseline condition, maximum heat release occurs at 6.4° ATDC. The timing obtained by heating the intake 20 K, 30 K and 40 K with respect to the base case is also included for comparison.

Ranking	Name	Chemical formula	Angle for maximum heat release rate, degrees	Advancement in combustion timing, degrees
	<b>Heating intake 40 K</b>		<b>-5.9</b>	<b>12.3</b>
1	Alkylhydroperoxide peroxy radical (See Fig. 1 for structure)	PC <sub>7</sub> H <sub>14</sub> OOH-QO <sub>2</sub>	-4.5	10.9
2	Alkylhydroperoxide peroxy radical (See Fig. 1 for structure)	NC <sub>7</sub> H <sub>14</sub> OOH-PO <sub>2</sub>	-4.5	10.9
3	Alkylhydroperoxide peroxy radical (See Fig. 1 for structure)	DC <sub>6</sub> H <sub>12</sub> OOH-EO <sub>2</sub>	-4.4	10.8
4	Alkylhydroperoxide peroxy radical (See Fig. 1 for structure)	FC <sub>6</sub> H <sub>12</sub> OOH-HO <sub>2</sub>	-4.4	10.8
5	Alkylhydroperoxide peroxy radical (See Fig. 1 for structure)	AC <sub>8</sub> H <sub>16</sub> OOH-CO <sub>2</sub>	-4.4	10.8
27	Ozone	O <sub>3</sub>	-4.2	10.6
	<b>Heating intake 30 K</b>		<b>-3.8</b>	<b>10.2</b>
81	Nitrosyl hydride	HNO	-3.4	9.8
103	Peroxy formic acid	HCO <sub>3</sub> H	-2.7	9.1
122	Ketohydroperoxide (See Fig. 1 for structure)	IC <sub>5</sub> KETCD	-2.2	8.6
204	Alkylhydroperoxide (See Fig. 1 for structure)	CC <sub>8</sub> H <sub>17</sub> O <sub>2</sub> H	-1.4	7.8
	<b>Heating intake 20 K</b>		<b>-1.4</b>	<b>7.8</b>
267	Hydrocarboxyl radical	HCO <sub>2</sub>	0.9	5.5
302	Nitric oxide	NO	2.1	4.3
342	Amino radical	NH <sub>2</sub>	2.6	3.8
369	Cyno radical	CN	5.5	1.1
370	Hydrogen peroxide	H <sub>2</sub> O <sub>2</sub>	5.5	1.1
	<b>No additive</b>		<b>6.4</b>	<b>0</b>
422	Hydrogen	H <sub>2</sub>	6.4	0
449	Ammonia	NH <sub>3</sub>	6.4	0
514	Carbon dioxide	CO <sub>2</sub>	6.4	0

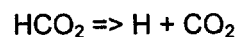
Since it is a radical, its stability during additive generation and storage would have to be evaluated for it to be considered as a practical additive.

The next series of additives which promote HCCI combustion contain the same molecular structure ROOH where R is a hydrocarbon or carbonyl structure. These include peroxy formic acid (additive 103, Table 5), the ketohydroperoxide group (e.g. additive 122), and the alkylhydroperoxide group (e.g. additive 204) and their example structures can be seen in Figure 9. The mechanism of their promoting effect is simply:



One reactive OH radical is produced for each additive molecule consumed. The RO<sub>2</sub> produced is also a radical and may lead to further promotion. For the

additive peroxy formic acid, the "RO<sub>2</sub>" is HCO<sub>2</sub> and is particularly reactive:



An OH radical and an H atom are produced for each additive molecule consumed. The second reaction shows why the HCO<sub>2</sub> radical is computed to be an effective additive itself (Table 5).

Since the additives with the structure ROOH are stable compounds and not radical species their lifetimes after generation and storage on board the vehicle are expected to be longer than the previously discussed radical species.

The additive NO is effective because it converts relatively unreactive HO<sub>2</sub> radicals produced during the compression stroke into reactive OH radicals, promoting ignition:



Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) would be expected to be a very effective additive because of its decomposition to form two reactive OH radicals:



However, the bond dissociation energy of H<sub>2</sub>O<sub>2</sub> is high (52 kcal/mole, 217 kJ/mole, corresponding to an activation temperature of 2615 K). This means that H<sub>2</sub>O<sub>2</sub> does not decompose in the compression stroke until the temperature reaches 900-1000 K, which is too late for hydrogen peroxide to be a highly effective additive (Table 5). The additives with the ROOH structure have bond dissociation energies of 37-46 kcal/mole. They decompose at temperatures below 900 K and very effectively promote the low temperature chemistry.

## CONCLUSION

This paper shows an evaluation of fuels and additives for HCCI combustion. The paper has three main parts. First, a list of candidate HCCI fuels is selected. For all the fuels in the list, operating conditions are determined that result in optimum performance under typical operation for a heavy-duty engine. Fuels are also characterized by presenting Log(p)-Log(T) maps for multiple fuels under HCCI conditions. The Log(p)-Log(T) maps illustrate important processes during HCCI engine operation, including compression, early chemical heat release and ignition. The paper also includes a ranking of many potential additives. Additives are ranked according to their capability to advance HCCI ignition. The main conclusions obtained from the paper are summarized next.

Operating conditions for satisfactory HCCI combustion (compression ratio, equivalence ratio and temperature) are limited by the characteristics of the fuel. Fuels with a relatively low octane number cannot operate at a high compression ratio unless the intake mixture is cooled below ambient temperature. Fuels with a high octane number may require considerable preheating to operate at a low compression ratio.

The efficiency and IMEP that can be obtained from an engine at a given compression ratio falls within a relatively narrow range for all the fuels considered in the analysis. However, within the narrow range significant differences are observed. Natural gas and methane have about 4% lower efficiency than other fuels because they have a higher equivalence ratio than the other fuels for a given compression ratio. As a result, the specific heat ratio ( $\gamma$ ), is lowest for methane and natural gas, resulting in lower engine efficiency. Hydrogen falls noticeably below the IMEP-compression ratio line followed by all the other fuels, mainly because burn duration is extremely short for hydrogen. Increasing the burn duration could potentially increase the power output that can be

obtained from an engine. However, no fuel was found that would result in a significantly extended HCCI combustion.

Log(p)-Log(T) maps were generated for four different fuels. These diagrams help visualize the effect of octane number and early heat release on HCCI operation. The maps show that fuels with equal research octane number (RON) may have considerably different heat release characteristics.

Several additives were identified that advance combustion by almost 11 crank angle degrees when added to the intake mixture at a concentration of 10 ppm. This is a big effect, equivalent to increasing the intake temperature by more than 30 K. The best additives are alkylhydroperoxide peroxy radicals, but the long-term stability of these compounds has to be demonstrated before they can be applied to engine control. Ozone is an excellent additive, and it is also stable and easy to manufacture on board a vehicle.

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